Blends of Poly(butylene terephthalate) with Co[poly(ethylene terephthalate-p-oxybenzoate)]: Crystallization Behaviors

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SYNOPSIS

Polyblends of poly(butylene terephthalate) (PBT) with four different types of co[poly(ethylene terephthalate-p-oxybenzoate)] copolyester, designated as P28, P46, P64, and P82, were prepared by melt-blending. The crystallization behaviors of the blends were then studied by differential scanning calorimetry and polarized optical microscopy (POM). Crystallization rate and temperature of neat PBT are increased when less than 10 wt % of P28 is blended. On the contrary, crystallization rate and temperature of neat PBT decrease when 10 wt % of P46, P64, or P82 copolyesters is blended. The crystallization behaviors of the blends are confirmed by the POM observations at the cooling cycles of the melts. On the other hand, melting endotherm onset temperature and melting peak width for all blends are comparable with those of neat PBT. These results imply that the stability and distribution of PBT crystallites in the blends are not significantly influenced by blending. The effects of POB content in the composition of the blends on the crystalline morphology were also presented. It is found that the structure of crystallites of the blends changed gradually with increasing the POB content in the composition of copolyester from lamellar to cross-like spherulite structures. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Poly(butylene terephthalate) (PBT), a high-performance, semicrystalline resin, is one of the toughest and most versatile of all engineering thermoplastics. Continued technological developments in alloying have extended the capabilities of the basic PBT resins and have led to an expanded acceptance in materials-consuming industries.[1] In order to enhance the ease of processing and the rapidity of crystallization rate, the crystallization behavior of this resin must be more intensively investigated.

On the other hand, polymer blends have recently become attractive both for industrial application and to academic interest. They have been found to be the main route more for the preparation of more convenient and available products than for developing new polymers through monomer synthesis and polymerization. Moreover, blending can improve properties and processibility of existing polymers and reduce costs to achieve performance/price balance. The inherent properties of the individual polymer components; the mode of dispersion; the shape, size, and orientation of phases; their interaction; and volume fractions were all important factors of the blends' behaviors. Most of the research on the PBT blends was concerned with compatibility.[2-8] The phase behavior of p-oxybenzoic acid–poly(ethylene terephthalate) (POB–PET)/PBT blend as revealed by differential scanning calorimetry (DSC) and by dynamic mechanical measurements is reported by Kimura and Porter[9] and Zadula and coworkers,[10] respectively. However, in the view of crystallization in our previous study,[11-12] we have found that an addition of the copolyesters (POB–PET) can accelerate the crystallization rate of PET in a manner similar to a nucleating agent. As a result, the crystallization behavior of PET in the blends might be influenced by the composition and amount of the copolyester blended.

EXPERIMENTAL

Materials

Four types of co[poly(ethylene terephthalate-p-oxybenzoate)] copolyesters, designated as P28, P46, P64, and P82, were synthesized according to the procedure reported in our previous study.[13] These copolyesters contain different POB/PET mole ratios, as shown in Table I; i.e., P28 in 20/80, P46 in 40/60, P64 in 60/40, and P82 in 80/20 mole ratios. PET and PBT were kindly supplied by the Far East Texile Co. (Taiwan). PET and PBT have an intrinsic viscosity value of 0.62 and 1.0 (dl/g), respectively. Intrinsic viscosity values were measured at 25°C in 40/60 phenol/tetrachloroethane (by weight ratio). The codes for each sample examined in this paper are listed in Tables I and II.

Blending Method

Copolyesters PET and PBT were dried at 70°C for 48 h in a vacuum oven prior to blending. The blends were prepared by melt-compounding on a Brabender Plasticorder with a batch-type roller mixer in various PBT/copolyester ratios (wt %). The samples were blended at temperature of 250°C for 8 min and a rotor

Table I Code of Copolyesters Synthesized

Copolyester (POB/PET)	Composition (Mole Ratio)	Code
POB/PET	20/80	P28
POB/PET	40/60	P46
POB/PET	60/40	P64
POB/PET	80/20	P82

Table II Weight Ratio and Conditions of Blends

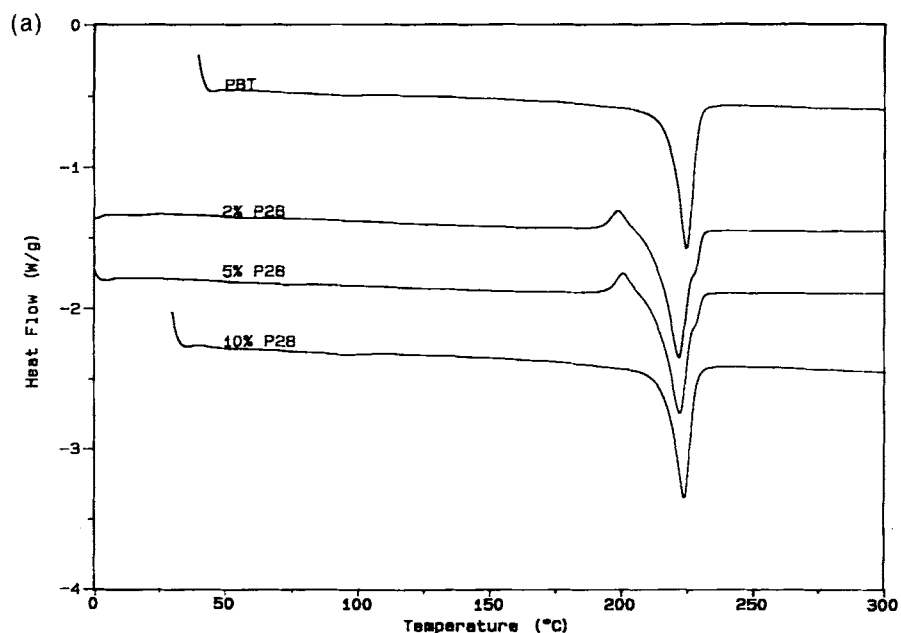| Weight Ratio (wt %)	Temperature of Blending (°C)	Time of Blending (min)
PBT (100)	250	8
P28/PBT (2/98)	250	8
P28/PBT (5/95)	250	8
P28/PBT (10/90)	250	8
P46/PBT (10/90)	250	8
P64/PBT (10/90)	250	8
P82/PBT (10/90)	250	8

Figure 1 (a) DSC curves of PBT and PBT/P28 blends for heating scan. (b) DSC curves of PBT and PBT/P28 blends for cooling scan.
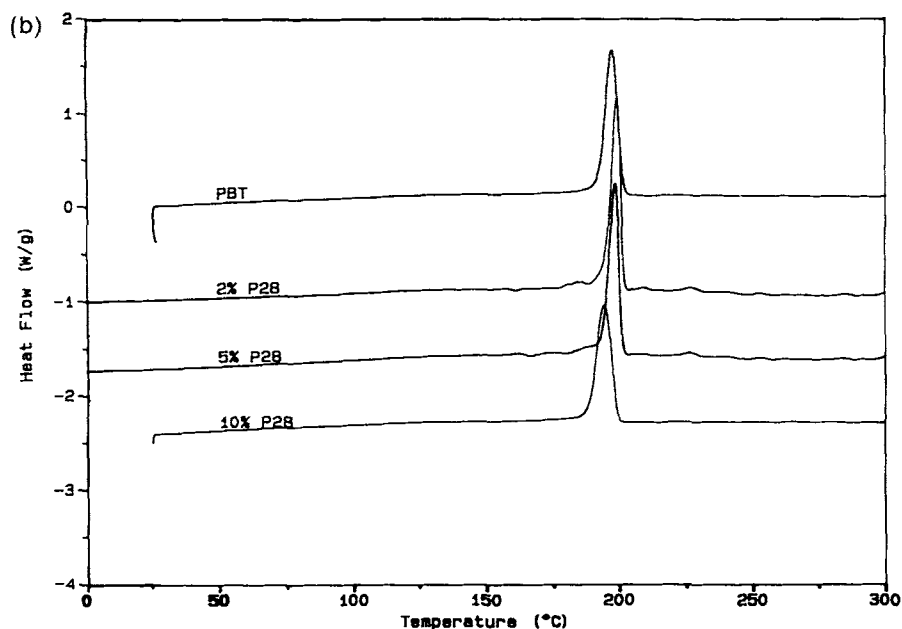
Figure 1 (*Continued from the previous page*)

speed of 30 rpm. After blending, the sample was taken from the mixer and immediately quenched in liquid nitrogen. Three compositions were prepared with PBT/P28 ratios of 98 : 2, 95 : 5, and 90 : 10 wt %. The PBT/P46, PBT/P64, and PBT/P82 were made, however, only at 90 : 10 ratio. The neat PBT was also subjected to identical processing in the Brabender mixer in order to nullify the effect of thermal history.

Differential Scanning Calorimetry

The quenched samples were vacuum dried at 70°C for 48 h prior to DSC measurement. The dry samples were reduced to about 0.5 mm in diameter by a cutting mill. The weight of all samples was kept at exactly 10 mg in DSC measurement using a Du Pont 2910. The samples were quickly heated to 300°C at a flow rate of 50cc/min under a nitrogen atmosphere, held for 3 min to destroy anisotropy, and then quenched in liquid nitrogen. After 3 min at the same condition, the quenched sample was heated to 305°C at a heating rate of 10°C/min, holding the sample at 305°C for 5 min and then cooling it at a rate of 10°C/min to 0°C.

Polarized Optical Microscopy (POM)

The morphology of blends was studied with a Zeiss polarized optical microscope (III). The sample was prepared by heating a piece of glass plate at above the melting temperature of the blends, and then

pressing the melts with another piece of hot glass plate so that it formed a sandwich, keeping the thin film inside. The sandwich was slowly cooled at room temperature. The photomicrographs of the films were taken at room temperature. Three types of film, i.e., PBT, PBT/2 wt % P28 blend and PBT/10 wt % P64 blend, were heated to 280°C at a heating rate of 10°C/min; the sample was held at 280°C for 3 min and then cooled at a rate of 10°C/min to 150°C. The photomicrographs of the three types of films at the appropriate temperatures in heating and cooling cycle were then taken. The incident polarizing light of the polarized optical microscope was at 90 degrees (magnification ×320).

RESULTS AND DISCUSSION

DSC Analysis

The curves of the DSC heating and cooling scans for PBT/P28 blends in different blending amounts of copolyesters are illustrated in Figure 1(a) and (b), respectively. Similarly, those for PBT/10 wt % copolyester blends are illustrated in Figure 2(a) and (b), respectively.

From the curves in the heating scans, we obtained the endothermic peaks, which did not show the clear glass transition temperatures (T_g); all PBT blends showed only a distinct crystallization exotherm peak in the cooling scans. The various melting and crys-

Table III   DSC Data of PBT Blends with Different Blending Ratios of P28

Composition PBT/P28 (wt %)	Melting				Crystallization				
	Onset T_m (°C)	ΔT_m (°C)	T_m (°C)	ΔH_f (J/g)	Onset T_c (°C)	ΔT_c (°C)	T_c (°C)	ΔH_c (J/g)	ΔH_c/time (J/g·sec)
100/0	204	30	224	49.65	203	18	197.5	52.96	0.471
98/2	206	26	222	55.99	203	14	199.3	52.26	0.622
95/5	207	26	222	49.66	202	15	198.5	48.76	0.554
90/10	206	27	224	47.45	201	20	194.3	49.02	0.436

tallization parameters determined from those scans are listed in Tables III and IV.

Blending with P28

As seen in Table III, the onset melting temperatures (T_m) of all PBT/P28 blends are little higher than that of neat PBT. Since this parameter is related to the least stability of crystallites, it can be supposed that the least stability of PBT crystallites is not significantly influenced by blending with 2–10 wt % P28 copolyesters. A similar result was seen at the width of melting (ΔT_m), which is related to the distribution of the size of crystallites. This result implies that the crystallization behavior was not much influenced when PBT was blended with 2–10 wt % P28 copolyesters.

The heat of fusion (ΔH_f) of 2 wt % blend was a little higher than that of neat PBT, whereas H_f of the 10 wt % blend was a little lower than that of neat PBT, and H_f of the 5 wt % blend was the same as that of neat PBT. The degree of crystallinity of

the blend is approximately in the linear relationship with the heat of fusion. The greater the heat of fusion, the higher the degree of crystallinity of a blend. However, a decrease in the degree of crystallinity was exhibited by the PBT blend with 10 wt % of P28. For convenience, the crystallization temperature (T_c) is defined as the temperature of the highest exotherm peak, while the crystallization rate is defined as the heat of crystallization in a unit of time $(\Delta H_c/\text{time})$. It was found that both crystallization temperature and crystallization rate of the blends with less than 5 wt % of P28 were higher than those of neat PBT. In other words, the crystallization rate of PBT was accelerated 1.32 and 1.18 times by blending 2 wt % and 5 wt % of P28 copolyester, respectively. Small quantities (less than 5 wt %) of P28 copolyester could act as nucleating agents for PBT resin but large quantities of P28 will destroy the symmetry of PBT and result in decreases of the ΔH_c, ΔH_f, and T_c, as seen in Table III. The PBT/2 wt % P28 blend exhibits the highest crystallization temperature and the fastest crystallization rate among all PBT/copolyesters blends.

Table IV   DSC Data of PBT Blends with 10 wt % Different Copolyesters

| Composition 10 wt % Copolyester	Melting				Crystallization				
	Onset T_m (°C)	ΔT_m (°C)	T_m (°C)	ΔH_f (J/g)	Onset T_c (°C)	ΔT_c (°C)	T_c (°C)	ΔH_c (J/g)	ΔH_c/time (J/g·sec)
PBT	204	30	224	49.65	203	18	197.5	52.96	0.471
PBT/P28	206	26	224	47.45	201	20	194.3	49.02	0.436
PBT/P46	207	28	224	42.94	198	19	189.4	48.28	0.414
PBT/P64	207	28	224	46.64	197	19	187.5	48.06	0.422
PBT/P82	206	30	224	43.46	202	18	195.9	47.61	0.439
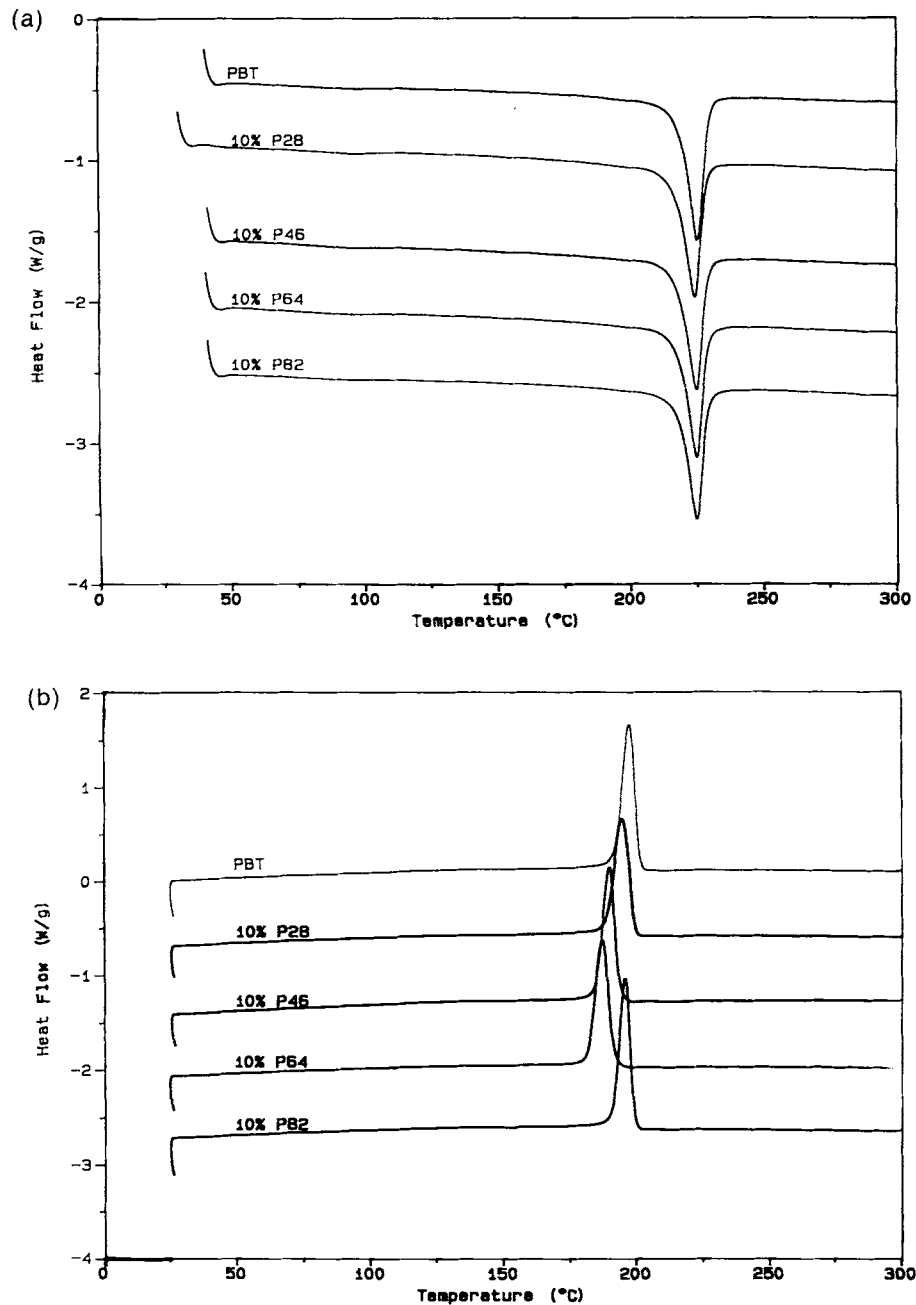
Figure 2 (a) DSC curves of PBT and PBT/10 wt % copolyester blends for heating scan.
(b) DSC curves of PBT and PBT/10 wt % copolyester blends for cooling scan.

Effects of Copolyester Composition

As seen in Table IV, the onset T_m of all PBT/10 wt % copolyesters are the same as that of neat PBT (224°C). The onset T_m of all blends are little higher than that of neat PBT. The ΔT_m of all blends are little lower than that of neat PBT. This result implies that the crystallization behavior was not much

influenced when PBT was blended with 10 wt % POB–PET copolyesters. No matter what type the copolyester is, the heats of fusion (ΔH_f) are decreased for all blends, meaning that the degree of crystallinity is decreased for all blends of PBT/10 wt % copolyesters. This is a reasonable phenomenon because a large-quantity addition of other species to a matrix polymer, in most conditions, will disorder

(a)

(b)

(c)

(d)
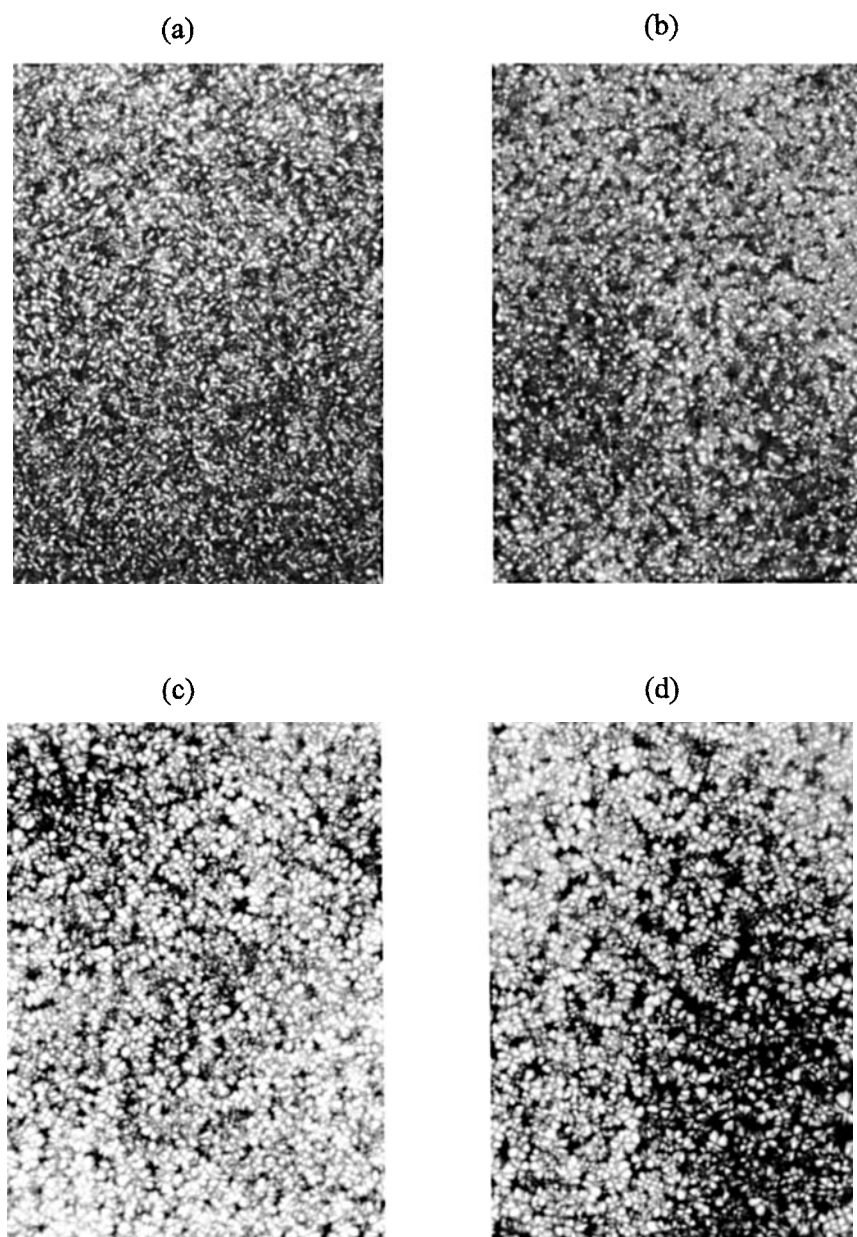
Figure 3 Polarized optical micrographs of PBT blended with different amounts of P28 at room temperature: (a) PBT; (b) 2 wt % P28 blend; (c) 5 wt % P28 blend; (d) 10 wt % P28 blend.

the arrangement of matrix molecules and influence the degree of crystallinity. The PBT/10 wt % P46 blend has the lowest H_f among all blends (see Table IV). It is well known that POB–PET copolyester exhibits the liquid crystal phase when POB composition in the copolyester is more than 60 mol %. It is also known that the crystalline nature of P46 copolyester is in the transition state between amor-

phous and liquid crystal texture. P64 and P82 co-polyesters show more orderly alignment than P46 copolyester does when the blends melt. The PBT/10 wt % P46 blend exhibits the smallest H_f and the slowest crystallization rate (see Table IV). On the other hand, crystallization rate and crystallization temperature of PBT are decreased if it is blended with 10 wt % copolyester.

(a)

(b)

(c)
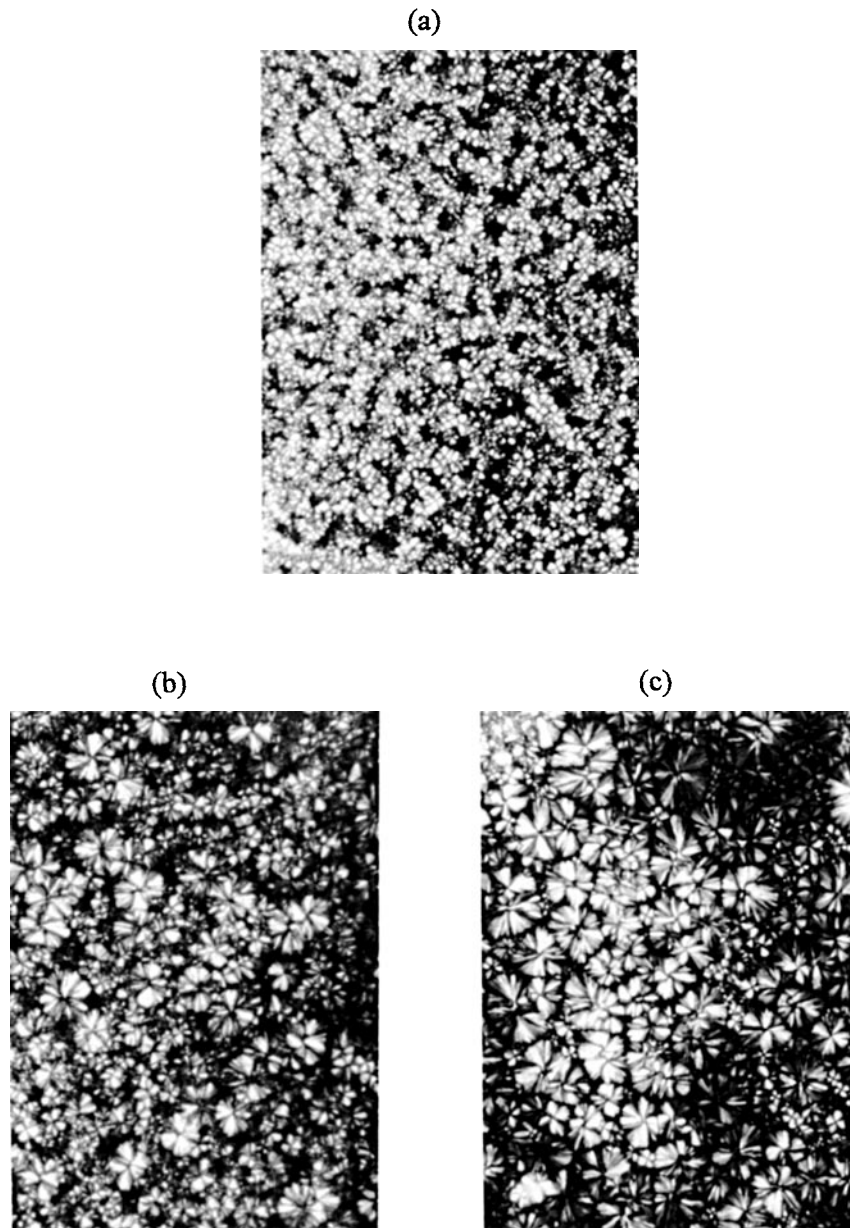
Figure 4   Polarized optical micrographs of PBT blended with 10 wt % different copolyester at room temperature: (a) 10 wt % P46 blend; (b) 10 wt % P64 blend; (c) 10 wt % P82 blend.
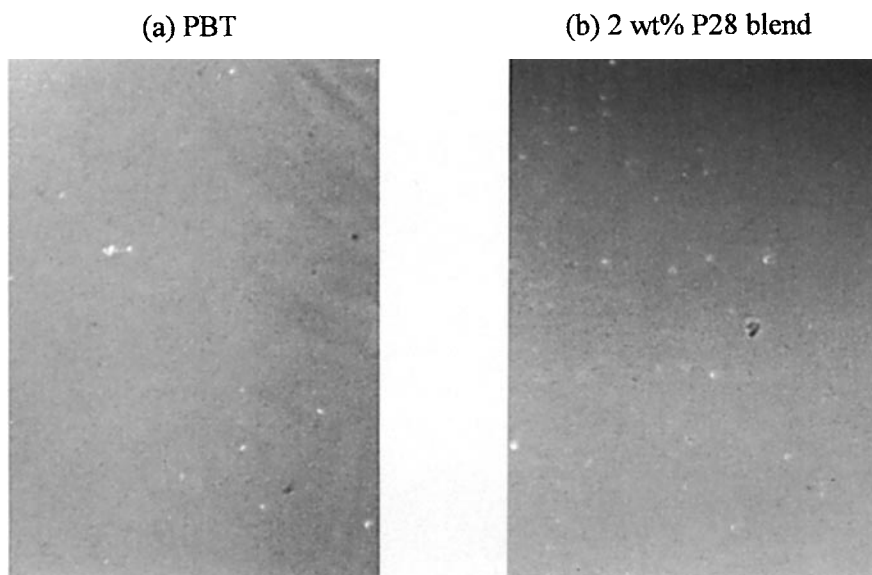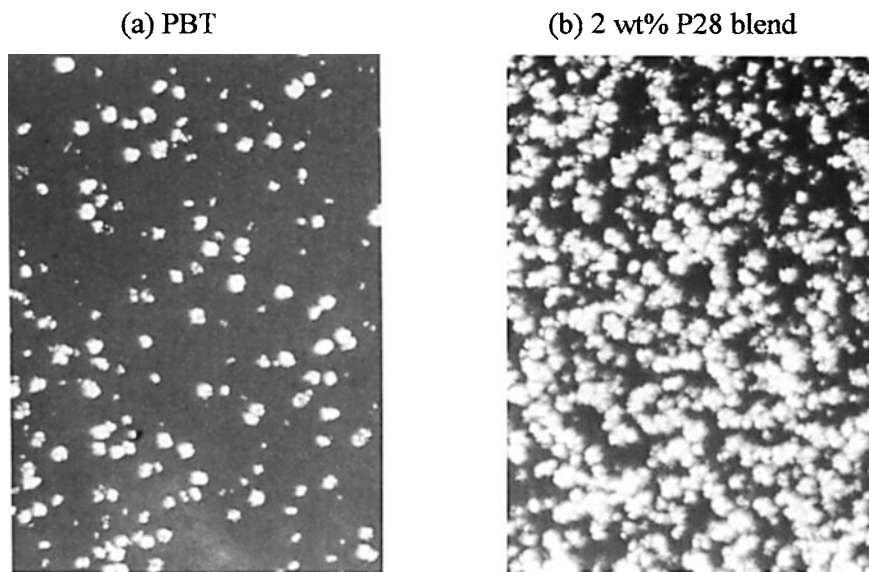
(a) PBT   (b) 2 wt% P28 blend

Figure 5 Comparison with the morphologies of crystallites between PBT and 2 wt %
P28 blend at 198°C in cooling cycle by POM observation: (a) PBT; (b) 2 wt % P28 blend.
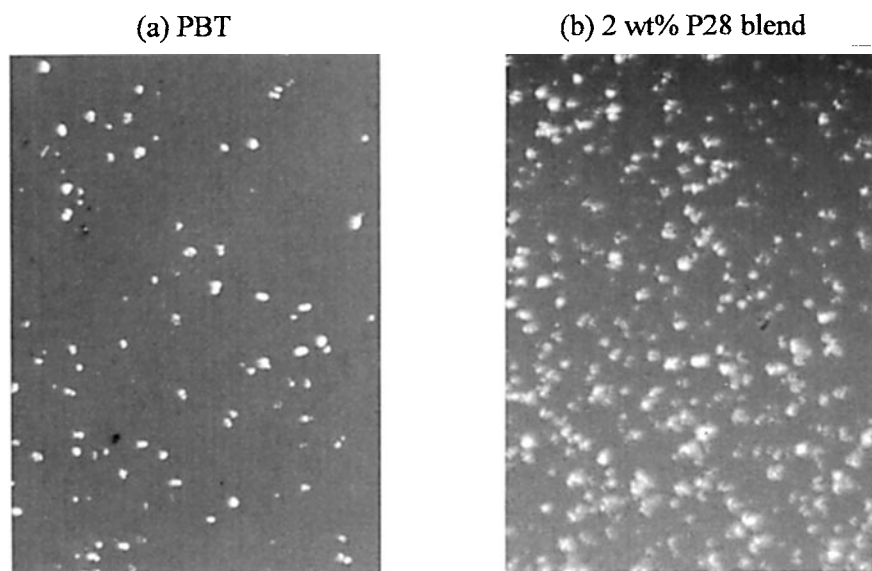
(a) PBT   (b) 2 wt% P28 blend

Figure 6 Comparison with the morphologies of crystallites between PBT and 2 wt %
P28 blend at 195°C in cooling cycle by POM observation: (a) PBT; (b) 2 wt % P28 blend.
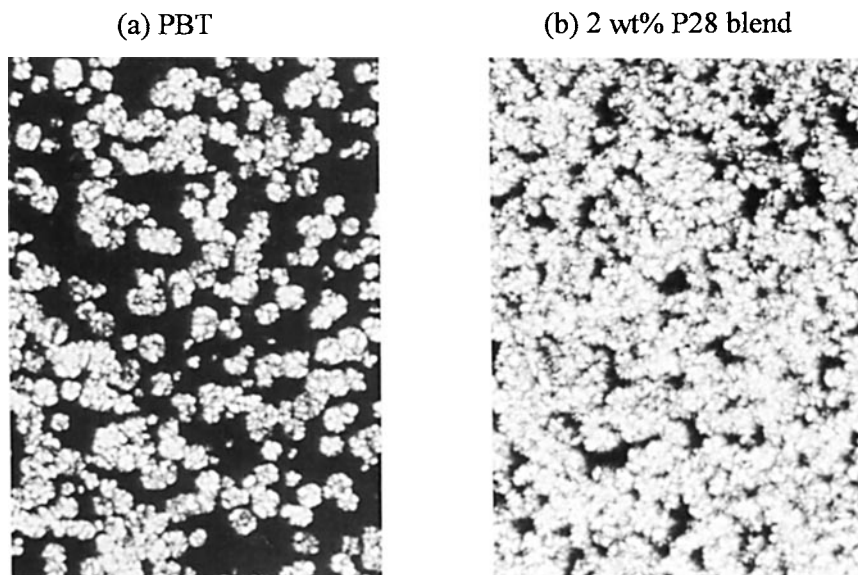
Figure 7 Comparison with the morphologies of crystallites between PBT and 2 wt %
P28 blend at 193°C in cooling cycle by POM observation: (a) PBT; (b) 2 wt % P28 blend.
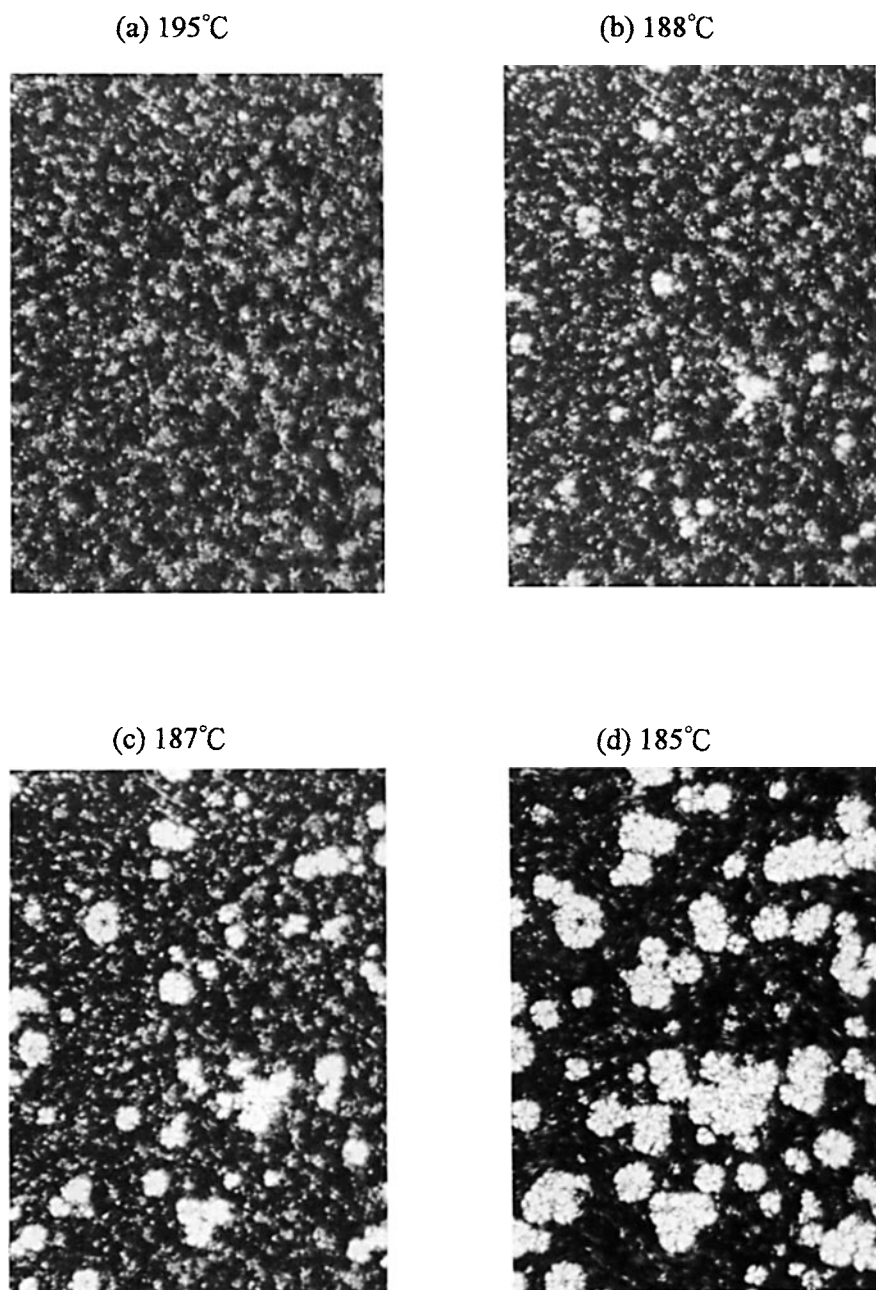

Figure 8 Comparison with the morphologies of crystallites between PBT and 2 wt %
P28 blend at 190°C in cooling cycle by POM observation: (a) PBT; (b) 2 wt % P28 blend.

(a) 195°C

(b) 188°C

(c) 187°C

(d) 185°C

Figure 9 Polarized optical micrographs of PBT/10 wt % P46 blend at different temperatures in the cooling cycle: (a) 195°C; (b) 188°C; (c) 187°C; (d) 185°C.

POM Analysis

Effects of Composition

POM was used to observe the crystalline texture of PBT blends. Figure 3(a) shows the spherulitic texture of neat PBT. Figures 3(b) to 3(d) show the crystalline texture for PBT blended with different amounts of P28. The morphology of the PBT/2 wt

% P28 blend represents the texture of spherulites [Fig. 3(b)]. As shown in Figures 3(c) and 3(d), for 5 wt % and 10 wt % P28 blends, respectively, the size of spherulites increases when the blended amount of P28 increases. In Figure 4(a), the patterns show smaller and closer spherulite textures for PBT/10 wt % P46 blends. In Figures 4(b) and 4(c), when PBT blended respectively with 10 wt % P64 and

P82, the crystallite domains become larger and form the snowflake-like pattern of perfect spherulites. The PBT blends' densities and crystallite diameters are listed in Table V. It seems that the size of the crystallites increases as the POB content in the blend increases, except in the PBT/10 wt % P46 blend. It could be summarized that density and size of the crystallites of PBT blends are influenced by the blending ratio and the composition of the co-polyesters. In PET/P28 blends, PET/2 wt % P28 exhibiting the smallest-diameter crystallites might be due to the increase in the nucleation site. In PET/10 wt % copolyester blends, on the other hand, the PET/10 wt % P46 blend exhibits the smallest-size crystallite (see Table V) and the slowest crystallization rate (see Table IV). This may result from the fact that crystallization in polymers involves the steps of primary nucleation and relatively rapid spherulite growth. The PET/2 wt % P28 blend might have a relatively slow spherulite growth. The density of crystallites of the blends decreases greatly when the POB composition of the copolyester increases from 60 (i.e., P64) to 80 mol % (i.e., P82) (see Table V).

Crystallization Rate Observation by POM

Figures 5 through 8 show the POMs of PBT/2 wt % P28 blend and neat PBT at the different temperatures. By comparing Figures 5 (at 198°C), 6 (at 195°C), 7 (at 193°C), and 8 (at 190°C), we see that the amount of crystallites of PBT/2 wt % P28 blend is always larger than neat PBT at the same temperature. These observations prove that the crystallization temperature and crystallization rate of PBT/2 wt % P28 blend are higher than those of neat PBT. Figure 9 shows the POM of PBT/10 wt % P46 blend in the cooling cycle. There is still no appearance of any crystallite of PBT but P46 phases (a bit colored) are observed at 195°C [Fig. 9(a)]; only a few crystallites appeared (in light white color) even at 188°C [Fig. 9(b)]. At 185°C, there first appeared many complete crystallites in the form of spherulites, in light white color [Fig. 9(d)]. The result indicates that the crystallization temperature and crystallization rate of 10 wt % P46 blend are much slow in comparison with those of neat PBT under the same cooling-cycle conditions.

CONCLUSION

It was detected from DSC analysis that the crystallization rate of PBT was accelerated by blending with P28 copolyester in 2-5 wt %. The PET/2 wt % P28 blend exhibited the highest crystallization

Table V   Effects of Blending Ratio and Composition on Density and Diameter of Crystallites of PBT Blends

	Density (Numbers/cm^2)	Diameter (d) (μm)	Δd
PBT	—*	1.5–6.9	5.4
2% P28	—*	2.2–9.7	7.5
5% P28	10.8	3.1–10.9	7.8
10% P28	16.3	3.1–14.6	11.5
10% P46	19.4	3.7–12.5	8.8
10% P64	4.1	5.6–25.0	19.4
10% P82	3.2	6.3–28.1	21.8

* —: cannot be counted exactly.

rate. This fact is also consistent with the results observed by POM. Small amounts (i.e., 2–5 wt %) of P28 copolyester could act as a nucleating agent for PBT resin. In addition, the morphology of the crystallite blends was influenced by both the blending ratio and the POB composition of the copolyesters.

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